

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) Jan 2014		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To) Jan 2014- Mar 2014	
4. TITLE AND SUBTITLE Thermal Decomposition Mechanism of HNNO ₂ H Dissociated from Mononitrobiuret and 1,5-Dinitrobiuret			5a. CONTRACT NUMBER FA9300-06-C-0023		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) H. Sun, G. L. Vaghjani			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER Q0RA		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680			8. PERFORMING ORGANIZATION REPORT NO.		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive Edwards AFB CA 93524-7048			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RQ-ED-TP-2014-038		
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for Public Release; Distribution Unlimited. PA#14112.					
13. SUPPLEMENTARY NOTES Technical paper presented at WSS Meeting, Cal Tech, CA, 24-25 Mar, 2014.					
14. ABSTRACT Mononitrobiuret (MNB) and 1,5-Dinitrobiuret (DNB) are, tetrazole-free, nitrogen-rich compounds, which have been reported as powerful new explosives. The initiation of thermal decomposition of MNB and DNB was found to involve an intra-molecular transfer of the H-atom from the central NH group to one of the adjacent nitro oxygens to eliminate the unstable intermediate, HNNO ₂ H, which undergoes further decomposition. In this work, we have investigated the thermal decomposition of HNNO ₂ H using multi-reference second-order perturbation theory and coupled-cluster theory. The following HNNO ₂ H decomposition pathways were found to be important. First, a direct N-OH bond fission occurs with a loose saddle point to form OH and cis-HNNO radicals. Second, an inversion of the aminylene H-atom elongates the N-OH bond due to repulsion between the aminylene H-atom and the hydroxyl H-atom, and this leads to N-OH bond fission to form OH and trans-HNNO radicals. Third, the thermodynamically stable products, N ₂ O + H ₂ O, are formed by a complex mechanism, which involves rotation of the N-OH bond, an H-atom shift from the hydroxyl H-atom to the nitric oxygen, and then migration of the aminylene H-atom to the hydroxyl O-atom, resulting in H ₂ O elimination with 50.4 kcal/mol of exothermicity.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 6	19a. NAME OF RESPONSIBLE PERSON G. Vaghjani
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NO (include area code) 5-5657

Spring 2014 Technical Meeting of the Western States Section of the Combustion Institute
Hosted by California Institute of Technology, March 23-25, 2014

Thermal Decomposition Mechanism of HNNO_2H Dissociated from Mononitrobiuret and 1,5-Dinitrobiuret

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Mononitrobiuret (MNB) and 1,5-Dinitrobiuret (DNB) are, tetrazole-free, nitrogen-rich compounds, which have been reported as powerful new explosives. The initiation of thermal decomposition of MNB and DNB was found to involve an intra-molecular transfer of the H-atom from the central NH group to one of the adjacent nitro oxygens to eliminate the unstable intermediate, HNNO_2H , which undergoes further decomposition. In this work, we have investigated the thermal decomposition of HNNO_2H using multi-reference second-order perturbation theory and coupled-cluster theory. The following HNNO_2H decomposition pathways were found to be important. First, a direct N–OH bond fission occurs with a loose saddle point to form OH and cis-HNNO radicals. Second, an inversion of the aminylene H-atom elongates the N–OH bond due to repulsion between the aminylene H-atom and the hydroxyl H-atom, and this leads to N–OH bond fission to form OH and trans-HNNO radicals. Third, the thermodynamically stable products, $\text{N}_2\text{O} + \text{H}_2\text{O}$, are formed by a complex mechanism, which involves rotation of the N–OH bond, an H-atom shift from the hydroxyl H-atom to the nitric oxygen, and then migration of the aminylene H-atom to the hydroxyl O-atom, resulting in H_2O elimination with 50.4 kcal/mol of exothermicity.

Keywords: Mononitrobiuret, 1,5-Dinitrobiuret, HNNO_2H , Decomposition, Kinetics.

1. Introduction

Mononitrobiuret (MNB) and 1,5-Dinitrobiuret (DNB) are, tetrazole-free, nitrogen-rich compounds, which have been reported as powerful new explosives that are comparable to the pentaerythritol tetranitrate (PETN), cyclotrimethylene trinitramine (RDX) and cyclotetra methylene-tetranitramine (HMX) based explosives.^{1,2} Klapötke et al. investigated the thermal decomposition of MNB and DNB using thermogravimetric analysis and differential scanning calorimetry, and found that MNB and DNB possess distinctive thermal behaviors.¹ In particular, MNB shows better thermal stability than DNB. Furthermore, it was proposed that the thermal decomposition of MNB and DNB is initiated by an intra-molecular S_{Ni} -reaction of the nitramide unit to form nitramide (H_2NNO_2) and corresponding unstable intermediate derivatives, which lead directly to isocyanic acid (HNCO), dinitrogen oxide (N_2O), carbon dioxide and water, as shown in Figure 1. The nitramide decomposes in the gas phase to N_2O and H_2O , where the latter reacts with gaseous HNCO to form NH_3 and CO_2 ; the same products were observed by Chambreau et al. in their studies on hypergolic ignition of ionic liquids.³

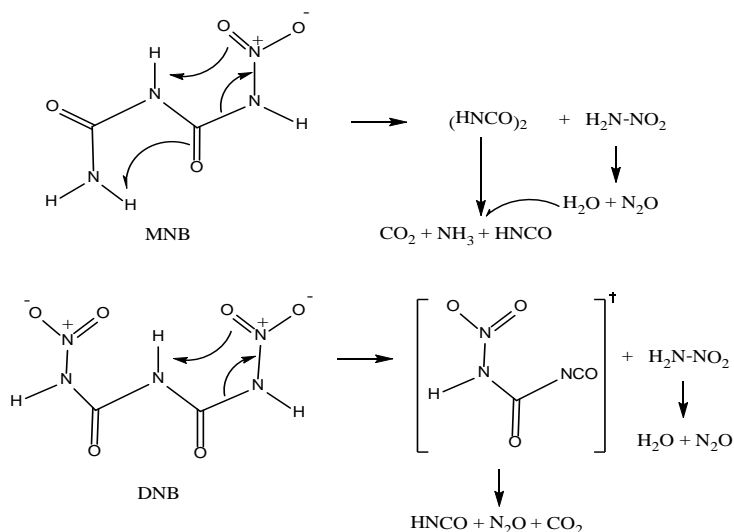


Figure 1. Proposed decomposition pathways of MNB and DNB by Klapötke et al. (2004)

Recently, direct dynamics trajectory simulations were performed by Liu et al. for the decomposition of DNB over the temperature range from 4000 to 6000 K to investigate the DNB thermal decomposition mechanisms.⁴ Their trajectory and RRKM results reveal several initial reaction paths relevant to the DNB thermal decomposition. First, their prediction for the predominant channel was consistent with the reaction scheme proposed by Klapötke et al.,¹ i.e., it corresponds to an elimination of HNNO_2H intermediate via a concerted mechanism with an energy barrier of $26.7 \text{ kcal mol}^{-1}$, the HNNO_2H subsequently isomerizes to stable nitramide (H_2NNO_2) via another energy barrier of $27.2 \text{ kcal mol}^{-1}$. Second, they reported two other decomposition channels which correspond to the elimination of NO_2 and H_2NNO_2 . For the NO_2 elimination path, they indicated a simple N—N bond scission process with an energy barrier of $38.3 \text{ kcal mol}^{-1}$; for the elimination of H_2NNO_2 , they suggested the reaction proceeds via twisting of the NHNO_2 group out of the molecular plane with an energy barrier of $6.0 \text{ kcal mol}^{-1}$, followed by a four-center intramolecular H-transfer transition state via an additional energy barrier of $43.1 \text{ kcal mol}^{-1}$. However, they reported that the reaction paths for NO_2 and H_2NNO_2 elimination below 1500 K are negligible due to the higher energy barrier or tight transition states, and only the path of HNNO_2H elimination is expected.

As a key intermediate from the decomposition of MNB and DNB, the HNNO_2H undergoes further decomposition to yield radicals and products with smaller molecular weights. The radicals produced can further react with the unreacted MNB or DNB fuel to induce ignition. However, the mechanism of HNNO_2H decomposition has not been reported. In this work, we have characterized the potential energy surface for the decomposition of HNNO_2H by using *ab initio* multi-reference second-order perturbation and coupled-cluster theories, and have identified the dominant reaction pathways.

2. Theoretical and Computational Details

For the HNNO_2H thermal decomposition, the multi-reference character of the wavefunction is significant for this only O, N, and H-atom containing system, especially for the bond breaking/forming process. Multi-reference second-order perturbation theory (CASPT2)⁵ with Dunning's augmented correlation consistent basis sets^{6,7} (aug-cc-pVDZ and aug-cc-pVTZ) was applied to optimize the geometries of the stationary points of the potential energy surface and to calculate the corresponding ro-vibrational frequencies. For the N—O bond fission in HNNO_2H , the state-averaged active space (4e, 3o) was chosen, which consists of two degenerated p orbitals of the OH and the p orbitals of N-atoms. For geometry optimization of HNNO_2H and its isomers, the active space consists of 12 electrons distributed among 9 orbitals: four σ orbitals including bonding and antibonding pairs of N—N and N—OH bonds, the π bonding orbitals of N=O double bond, the π antibonding orbitals among all the heavy atoms, the delocalized lone pair p orbital on the nitric oxygen, the lone pair p orbital on the hydroxy oxygen, and the lone pair p orbitals on the amino nitrogen and the nitric oxygen.

Except for the bond fission reactions, the stationary point energies of the potential energy surface were further obtained from spin restricted coupled-cluster theories with single and double excitations, and correction for triple excitations. Specifically, the CCSD(T) calculations employed the correlation-consistent, polarized-valence, triplet- ξ (cc-pVTZ) and quadruple- ξ (cc-pVQZ) basis sets of Dunning.^{6,7} The energies were then extrapolated to the complete basis set (cc-pV ∞ Z) limit by the asymptotic form.^{8,9} Electronic structure calculations were performed using the Molpro¹⁰ quantum chemistry package.

3. Results and Discussion

Figure 2 shows the potential energy surface of HNNO_2H decomposition characterized by using the CASPT2 and CCSD(T) *ab initio* methods. The thermal decomposition of HNNO_2H proceeds via a complex reaction process. It was found that the HNNO_2H intermediate has three stable rotational conformers. Here, the conformer dissociating directly from MNB or DNB, is named as $\text{HNNO}_2\text{H-1}$. A direct N—OH bond fission of the $\text{HNNO}_2\text{H-1}$ occurs via TS1 with a loose geometry ($E_a = 39.97$ kcal/mol) to form an H-bonded complex which dissociates to OH and cis-HNNO radicals. The cis-HNNO radical undergoes dissociation to yield H + N_2O , and also undergoes an exothermic 1,3-H shift to yield an OH radical and N_2 as the products. Furthermore, inversion of the aminylene H-atom in the $\text{HNNO}_2\text{H-1}$ via TS2 ($E_a = 30.11$ kcal/mol) elongates the N—OH bond due to repulsion between the aminylene H-atom and the hydroxyl H-atom, and facilitates N—OH bond fission to form trans-HNNO.

The $\text{HNNO}_2\text{H-1}$ also undergoes isomerization reaction via a four-member-ring transition state TS3 ($E_a = 28.87$ kcal/mol) to the nitramide (NH_2NO_2), which can dissociate to $\text{NH}_2 + \text{NO}_2$ or to $\text{NO} + \text{H}_2\text{NO}$ via TS5 ($E_a = 30.07$ kcal/mol) by a nitro–nitrite rearrangement.

An inversion of the hydroxyl H-atom in the $\text{HNNO}_2\text{H-1}$ via TS4 ($E_a = 5.59$ kcal/mol) forms the conformer $\text{HNNO}_2\text{H-2}$, whose energy is slightly lower than that of the $\text{HNNO}_2\text{H-1}$ conformer. The $\text{HNNO}_2\text{H-2}$ undergoes N—OH bond fission via TS6 with a loose geometry ($E_a = 40.21$ kcal/mol)

to form an H-bonded complex, which subsequently dissociates to OH and cis-HNNO radicals. The HNNO₂H-2 also undergoes isomerization to form the HNNO₂H-3 conformer by an H-atom shift of the hydroxyl H-atom to the nitric oxygen via TS7 ($E_a = 26.24$ kcal/mol). In the HNNO₂H-3 conformer, migration of the aminylene H-atom to the hydroxyl O-atom leads to elimination of H₂O ($E_a = 30.78$ kcal/mol) with a reaction exothermicity of 50.37 kcal/mol.

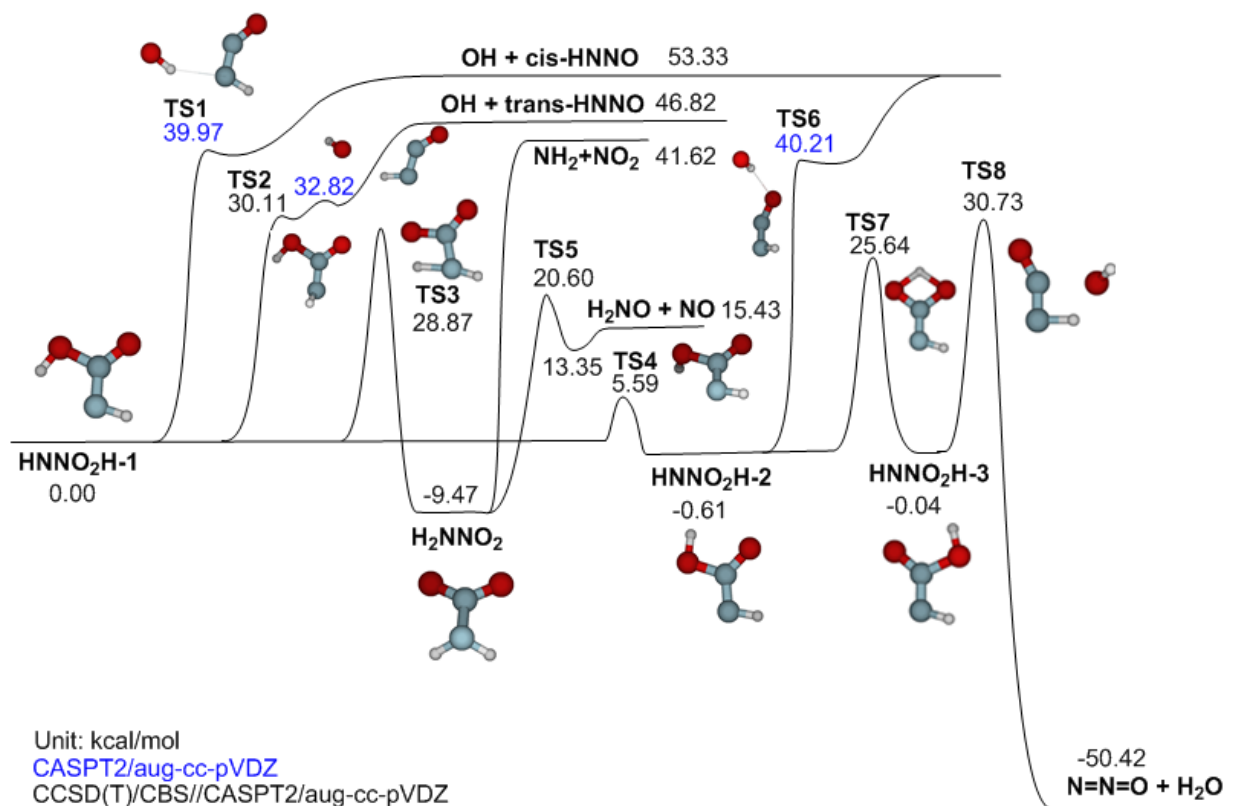


Figure 2: Potential energy surface for HNNO₂H decomposition. Energies are zero-point corrected and relative to that of the entrance channel at 0 K.

4. Conclusions

The thermal decomposition mechanism for HNNO₂H produced from mononitrobiuret and 1,5-dinitrobiuret decomposition was investigated by *ab initio* multi-reference second-order perturbation and coupled-cluster theories. Three reaction pathways were found to be important in the decomposition of HNNO₂H. First, a direct N–OH bond fission occurs with a loose saddle point to form OH and cis-HNNO radicals. Second, an inversion of the aminylene H-atom elongates the N–OH bond due to repulsion between the aminylene H-atom and the hydroxyl H-atom, and leads to N–OH bond fission to form OH and trans-HNNO radicals. Third, the thermodynamically stable products, N₂O + H₂O, are formed by a complex mechanism, which involves rotation of the N–OH bond, an H-atom shift from the hydroxyl H-atom to the nitric oxygen, and then migration of the aminylene H-atom to the hydroxyl O-atom with an overall reaction exothermicity of 50.4 kcal/mol.

Acknowledgements

The National Research Council is thanked for the Senior Research Associateship Award to H. Sun at the Air Force Research Laboratory, Edwards AFB under Contract No. FA9550-12-d-0001. This research was performed using resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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